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ON THE RAMAN SPECTRA OF A FEW NITRILES AT LOW TEMPERATURES

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Plate V

ABSTRACT. The Raman spectra of acetonitrile, propionitrile and benzonitrile have been investigated in the liquid and solid states and also the polarisation of the lines has been studied. The line due to C≡N deformation oscillation seems to be weakened and the frequency of the line due to C≡N valence oscillation diminishes in the solid state. The lines due to C–H valence oscillations also undergo changes in structure and intensity. No new line appears in the low-frequency region in the case of the two aliphatic nitriles but one such line appears in the case of benzo nitrile in the solid state. It is suggested that these changes in the Raman spectra may be due to formation of strongly associated molecules in the solid state.

INTRODUCTION

In continuation of the previous work by the present author in collaboration with Sirkar (1943, 1045, 1046a, 1946b) on Raman spectra of organic compounds in the solid state at low temperatures, the Raman spectra of three nitriles, *e.g.*, acetonitrile, propionitrile and benzonitrile have been studied in the solid state at low temperatures. It has already been observed that with the solidification of organic liquids at low temperatures, some changes in the Raman spectra take place. These three compounds have been chosen in the present investigation to find out whether the presence of the benzene ring has any influence on the appearance of the new lines in the low frequency region which have been observed in the case of benzene and some of its substituted compounds by previous authors and also by Sirkar and Bishui (1946). Further, the Raman spectra of these three liquids had been studied only by a few authors and the data regarding the polarisation of the Raman lines were not known for two of them. Hence this investigation was undertaken to study the Raman spectra in the liquid and solid states and also the polarisation of the Raman lines in all these cases, in order to understand the significance of the changes which are observed in the Raman spectra with the solidification of these liquids.

EXPERIMENTAL

Pure liquids were taken from Kahlbaum's original packings and were redistilled in vacuum. The technique used was almost the same as that developed for studying the Raman spectra of substances at low temperatures by

Sirkar and Bishui (1943), but slight modifications were introduced. The liquid distilled in vacuum was put in a long Pyrex tube passing through a cork which was fitted into the mouth of a transparent Dewar vessel of Pyrex glass placed in a vertical position. A narrow Pyrex glass tube, bent twice at right angles, the horizontal portion of which was double-walled and the annular portion of which had been evacuated and sealed previously was used for introducing liquid oxygen into this Dewar vessel. One of the vertical limbs of the tube was dipped into the liquid oxygen contained in a big metallic Dewar vessel and the other end passed through the cork fitting in the mouth of the transparent Dewar vessel. Another narrow glass tube bent at right angles was fitted in the cork in such a way that one of its ends lay about an inch below the cork, while the other end was connected through a stopcock and a reservoir to a Cenco Hyvac oil pump. When this vacuum pump was started and the stopcock was opened, the liquid oxygen from the metallic Dewar vessel came slowly and was collected in the lower part of the transparent Dewar vessel. The flow stopped as soon as the stopcock was closed. In this way an atmosphere of liquid oxygen vapour almost with a steady range of temperatures was maintained within the transparent Dewar vessel. A Pyrex tube containing the liquid was held with its bottom just above the surface of liquid oxygen. The apparatus is shown in figure 1. The advantage

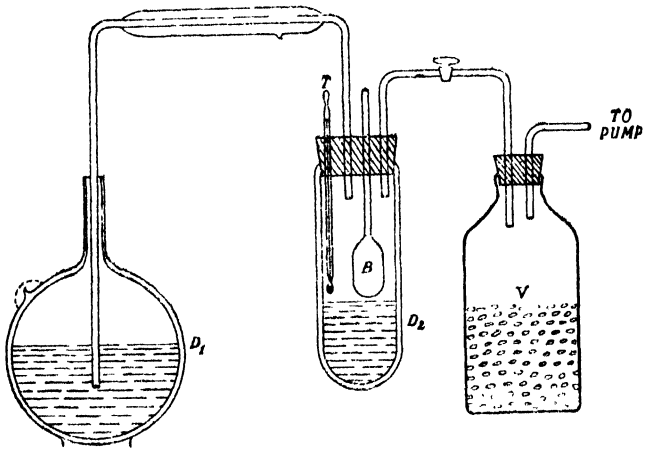

FIG. 1

of this method over the previous one was that this time the light was not absorbed by the liquid oxygen and consequently the time of exposure was much reduced. With this arrangement it was possible to continue the work during the rainy season even when the humidity was as high as 90%. In order to have a constant temperatures at a certain depth in the transparent Dewar vessel care was taken to maintain the level of the liquid oxygen in it at a particular height. A pentane thermometer was used to record the temperature of the solidified substance. The temperature was different at

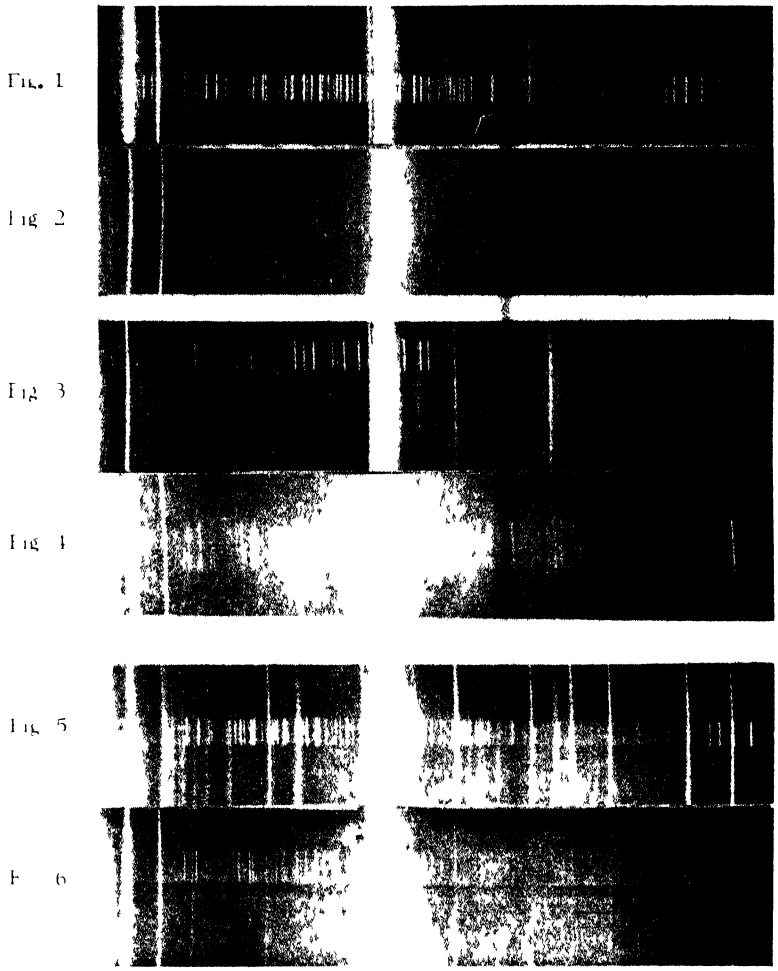

Fig	1	Acetonitrile	at about	+ 30°C.
	2	,,	,	−150 C
,,	3	Propionitrile	, ,,	+ 30 C
,,	4		,	−150 C
,,	5	Benzonitrile	, ,,	+ 30 C
,,	6		, ,	−150 C

ifferent heights above the surface of the liquid oxygen and the mean was observed.

Suitable portions of the Dewar vessel were blackened and the substance was illuminated with two vertical mercury vapour lamps, the light being focussed with the help of two six-inch glass condensers. The scattered light emerged through a window on one side.

A Fuess spectrograph having optical parts of glass was used in the present investigation. It has dispersion of about 14 A.U. per mm. in the region of 4046 A.U. A blue-violet glass filter was placed in the path of incident light in order to diminish the intensity of the continuous background in the region on long wavelength side of 4358 A.U. The polarisation of the Raman lines due to the liquid state was studied in each case by photographing simultaneously the spectra of the vertical and horizontal components of the scattered light with the help of a double image prism. Light from a mercury arc focussed with the help of the condenser was used as the incident light in this case also. The spectrograms, therefore, only indicated whether any Raman line was partially polarised or completely depolarised and no attempt has been made to measure the absolute values of factor of depolarisation accurately. In the case of the lines which are totally depolarised, the horizontal component appears stronger than the vertical component because the latter is reduced in intensity due to reflections at the surfaces of the prism in the spectrograph, and this criterion helped to identify the totally depolarised lines.

RESULTS AND DISCUSSIONS

The results obtained are given in tables I, II, and III. The first column of each table contains the results reported by some of the previous workers. The letters P and D denote polarised and totally depolarised ($\rho=6/7$) respectively. The approximate visually estimated intensities are given in the parentheses. The data for the solid at about $-150°$ C obtained in the present investigation are given in the last column. Some of the spectrograms are reproduced in Plate V.

Acetonitrile.—The Raman spectrum of acetonitrile in the liquid state was studied formerly by Dadieu and Kohlraush (1929), Pal and Sengupta (1930), and Petrikaln and Hochberg (1929), but the polarisation was not studied before. The data reported by Magat (1934) have been inserted in the first column of Table I, for comparison. The frequencies of some of the lines reported by previous workers are a little lower than those observed in the present investigation. The lines at 2294 cm^{-1} and 2731 cm^{-1} observed in the present investigation were not reported by the previous workers. The line at 384 cm^{-1} due to C≡N deformation oscillation seems to be weakened, and the line at 2731 cm^{-1} due to C–H valence oscillation vanishes in the solid state at low temperature. The most intense line at 2256 cm^{-1} due to C≡N valence oscillation is accompanied by the weak satellite at 2294 cm^{-1}

in the liquid state. Although this satellite was not reported by earlier workers, it is definitely present in the spectrogram reproduced in Plate V. This line may be due to the formation of associated molecules through C≡N bond and such association of molecules in the liquid state is probable in the present case, because the molecule is strongly polar and small in size. According to group theory CH_3CN molecule should yield four polarised and four totally depolarised Raman lines. The results obtained in the present investigation regarding the polarisation show that there are five polarised and three

TABLE I

Acetonitrile. C_2H_3N

Liquid at about 32°C		Solid at about −150°C Present author
Magat (1934)	Present author	
377 (3)	384 (5) e, k ; D	386 (od)
917 (3)	918 (4) e, k ; P	910 (ob)
1230 —		
1367 (2)	1370 (3b) e, k, P	1370 (1)
1417 (0)		
	1450(ob) e, k, P	
2249 (3)	2256(10) e, i, o, p, q ; P	2243 (4)
	2294(1) e, k ; P	2290 (0)
	2731(1) e, k ; ?	—
2941 (2)	2942(10) e, i, k, o, p, q ; P	2937 (5s)
2996 (1)	3004(4b) e, k ;D	3011 (4s)

TABLE II

Propionitrile. C_3H_5CN

Liquid at about 32°C		Solid at about −150°C Present author
Howlett (1931)	Present author	
220 (F)	218(4) ± e, ± k ; D	118(1)
		222(1)
370 (?)	377(3b) e ; D	V
540 f)	549 2) e, k ; P	552(0) e, k
	674(2) e, k ; P	674'2 e, k
840 (f)	845(5) e, k ; P	846 1) e, k
990 ..	...	.
	1005(3) e, k ; P	1010 1) e, k
1080 (f)	1075(3) e, k ; P	1072(1) e, k
1260 (f)	1260(2) k ; P	1260(1) k
1310 (f)	1316(2) k, D	1316(1) k
1430 (f)	1432(3) e, k ; D	1421(1) k
1470 (f)	1472(3) e, k ; D	V
2240 (f)	2250(10) e, k, o, p, q ; P	2242(3) e, k, o, p, q
2900 f)	2900(4) e, k, o, p, q ; P	2900(2) e, k, o, p, q
2950 (f)	2948(10) e, i, k, o, p, q ; P	2950(5X) e, i, k, o, p, q
		2970(3) e, k, o, p, q
3000 (f)	2997(4) e, k, o, p, q ; D	2993(3) e, k, o, p q

TABLE III

Benzonitrile. C_6H_5CN

Liquid at about 32°C		Solid at about −150°C Present author
Magat	Present author	
170(8) 6/7	174(3b) e, D	94(4) k
380(2) 0.36	380(2) e, D	
	407(1) e k : ?	
460(6) ...	463(5) e, k , P	459(1) k
549(5) ...	556(4) e, k ; D	555(0) e, k,
621(5) 6/7	630(5) e, k , D	630(1)
752(3) 0.15	755(4) e, k ; P	749(0)
765(5)	769(4) e, k ; P	764(0)
	809(1) e, k , P	. ..
	855(1) e, k ; ?	
998(5) 0.04	996(8s) e, k ; P	996 (5s)
1023(3) .	1024(3) e, k ; P	
1178(8) ...	1172(2s) e, k ; D	1172 (2)
	1184(2s) e, k : P	1182 (2)
1190(8) 0.24	1197(3s) e, k ; P	V
1310(1) ..		
1353(0) ...		
	1430(1b) e ; D	
1447(1) ...	1453(1) e, k ; D	
1493(2) ...	1498 1) e, k, D	
	1540(0) e, k, ?	
1596(10) 6/7	1601(10) e, k ; D	1595 (5) e, k
	2176(1) e, k, P	
2225(12) 0.23	2232(10) e, k, p	2226(5) e, k
		3060(2) e, k
3068(8) 0.30	3070(1) e, k, p, q ; P	3068(4) e, k
3146(1) ...	3146(1) e, k ; P	3146(0) e
3196... ...	3197(1) e, k ; P	3197(0) e.

depolarised lines. Evidently one of the depolarised lines is too weak to be recorded and the line at 2294 cm^{-1} which is polarised is probably not due to the single molecule.

In the solid state at about $-150°C$ the substance does not yield any new Raman lines in the low frequency region and it is observed that some of the prominent Raman lines of the single molecule undergo changes in frequencies and intensities at this low temperature. For instance, the lines at 918 cm^{-1}, 2256 cm^{-1} shift to 910 cm^{-1} and 2243 cm^{-1} respectively in the solid state. These lines being due to the C–C and C≡N valence oscillations this diminution of the frequencies shows the influence of intermolecular field in the solid state on these bonds. Another remarkable change observed is the enhancement of the intensity of the line 3004 cm^{-1} in the solid state. This line is due to the antisymmetric C–H valence oscillation.

Propionitrile.—The Raman spectrum of propionitrile in the liquid state was studied formerly by Dadieu and Kohlraush (1930) and Howlett (1931). The results reported by the latter author have been included in the first column of Table II for comparison. The lines at 674 cm^{-1}, 1075 cm^{-1} were not observed by the previous workers. No satellite in the neighbourhood of C≡N vibration is observed in this case. There are six totally depolarised Raman lines in the Raman spectrum of propionitrile. Hence the molecule has a symmetry element which is probably a plane of symmetry.

In the solid state at about $-150°C$ this substance also does not yield any new Raman lines in the low frequency region and it was observed that the line 377 cm^{-1} due to the C≡N deformation oscillation and 1472 cm^{-1} due to C–H deformation oscillation in the liquid state vanish completely in the solid state at low temperature. It can be seen from Table II that no other remarkable change takes place in the frequencies of the remaining prominent Raman lines, when the liquid is solidified at about $-150°C$, excepting the changes occurring in the C–H vibrations. The line at 2948 cm^{-1} due to the liquid is split up into two lines at 2950 cm^{-1}, 2970 cm^{-1} in the solid state at low temperature. This suggests that some change in the structure of the CH_3- group takes place in the solid state at low temperature, and this may be due to formation of a loose linkage through this group.

Benzonitrile.—The Raman spectrum of benzonitrile in the liquid state was studied by Kohlraüsh and Pongratz (19, 2) and Simons (1932). The results reported previously (Magat, 1934) have been included in the first column of Table III for comparison. The lines at 407 cm^{-1}, 809 cm^{-1}, 855 cm^{-1}, 1430 cm^{-1} and 2176 cm^{-1} due to the liquid observed in the present investigation were not reported by the previous workers. The presence of the satellite 2176 cm^{-1} of the C≡N vibration 2276 cm^{-1} has been verified by observing a satellite of the line 2276 cm^{-1} excited by 4046A. In this case also this line may be due to formation of associated pairs of molecules in the liquid state.

In the solid state at about $-150°C$ the substance yielded a new Raman line at 94 cm^{-1} in the low frequency region and it was observed that some of

the prominent Raman lines of the single molecule undergo changes in frequencies and intensities at the low temperature. It was also observed that some of the lines due to the liquid completely vanish in the solid state at low temperature. The line at 380 cm^{-1} due to $C\equiv N$ deformation oscillation disappears in the solid state. The presence of the line at 2176 cm^{-1} in the solid state could not be definitely established.

Since the Raman line due to $C\equiv N$ valence oscillation appears in the solid state with undiminished intensity while the intensity of the line due to the $C\equiv N$ deformation oscillation is practically absent in the solid state, it seems that this oscillation is restricted in the solid state. As this line is totally depolarised its intensity cannot be diminished by transmission through the mass of the crystal. Thus this fact is definitely an example of restriction on certain mode of vibration in the solid state.

Thus three interesting facts emerge out from the study of the Raman spectra of these three nitriles. First, the line due to $C\equiv N$ deformation oscillation becomes extremely weak in the solid state and the frequency of $C\equiv N$ valence oscillation diminishes slightly in the solid state. Secondly, there appear no new lines in the low frequency region in the spectra of the two aliphatic nitriles in the solid state at low temperature, but in the case of benzonitrile one new line appears at 94 cm^{-1}. Thirdly, the $C-H$ valence oscillations either undergo changes in intensity or are split up into components in the solid state. From the investigations of the Raman spectra of aliphatic and aromatic organic compounds at low temperatures made by Sirkar and Bishui (1943, 1945, 1946a, 1946b) previously, it was observed that new lines appear in the low frequency region in the case of all benzene compounds without fail, whereas in the case of many aliphatic compounds these new Raman lines do not appear in the low frequency region in the solid state at low temperatures. This peculiar behaviour of benzene compounds may be due to the presence of double bonds which are not wholly saturated in the benzene ring. Probably there is some tendency for the formation of associated molecules even in the liquid state and when the benzene compounds are solidified at the low temperature the molecules come closer and closer and probably they finally form strongly associated groups of molecules. Thus the appearance of new Raman lines in the low frequency region in the case of all the benzene compounds may be due to the formation of such strongly associated molecules in the solid state through carbon bonds. The changes in the lines due to $C-H$ valence oscillations with the solidification of the two aliphatic nitriles studied may be due to the formation of such associated molecules through the hydrogen bond which may not yield sharp lines but may produce diffuse bands which are difficult to detect.

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